

means of nitration were still functioning satisfactorily after 140,000 cycles.

4. A cylinder piston was geometry-tested. The piston was made of teflon and the cylinders were treated by oxidation, anodization and nitration. Untreated cylinders were also tested. The untreated cylinders and anodized cylinders malfunctioned almost immediately due to cutting. The oxidized cylinders in some cases functioned satisfactorily for a considerable time with good sealing and low wear, whereas in other cases they malfunctioned at an early stage. This may be explained by the poor mechanical stability and negligible hardness of the thin oxide layer. The nitride obtained with the nitration process described above functioned perfectly reliably over a long period of time if it was pre-polished (see FIG. 4) in order to avoid wear on the relatively soft seal. This surface never malfunctioned.

A new vacuum system for nitration has been constructed. In FIG. 1, 1 designates a furnace + furnace tube, 2 pressure control, 3 mass flow control, 4 gas entering, 5 valve, 6 needle valve, 7 vacuum pump and 8 gas leaving. The central part of the system is the furnace 1 which in fact consists of three part furnaces and six heating elements. This is in order to obtain a long and uniform temperature profile. The temperature varies by at most seven degrees within a length of 50 cm and 3 degrees within a length of 30 cm. A uniform temperature profile is necessary in order to avoid variations in the thickness of the titanium nitride layer. A long heating zone is also important so that the gas phase can be activated before coating occurs.

The temperature control occurs automatically and each furnace part can be controlled independently of the other two. The desired temperature is set with the aid of control units, thermoelements sensing the temperature, which is then controlled by thyristors. Pressure and gas flow are also controlled automatically after setting. The pressure is set by means of a needle valve 6, to just below the desired temperature. The pressure control then regulates the gas pressure by dosing a sufficient quantity of gas 4.

The furnace tube consists of quartz glass and has a diameter of 80 mm and length of about 110 cm. Quartz glass will withstand temperatures up to about 1100° C. The rest of the equipment consists of stainless steel except for the end connections to the furnace tube, which are made of aluminum. Water-cooling is required to protect these end connections from the heat radiating from the furnace.

The equipment must fulfil the highest tightness requirements. With the volume mentioned above, the leakage rate may not exceed about 50 millitorr/hour if the surface-converted layer is to obtain high purity, hardness and adhesion. Other mechanical properties of the layer may also be adversely affected if any leakage occurs. (A more brittle layer, poorer resistance to fatigue and higher friction may be obtained, for instance.)

The material according to the invention is suitable for joint prostheses. Thanks to the unique biocompatibility properties of titanium (fuses with bone marrow, no precipitation caused by exposure to body liquids) it is an extremely suitable material for use in joint prostheses (it is also currently used for this purpose). To obtain the requisite strength the alloy Ti-6Al-4V must be used. This alloy is also easier to work. However, from the biological point of view, it is inadvisable to expose body liquids or bone marrow to alloys containing Al since

this may easily result in toxic (allergic) reactions after protracted use, and the body will then reject the prosthesis. The method according to the invention for surface conversion of titanium and titanium alloys gives strong depletion of the alloying elements in the surface-converted layer and pure titanium nitride is obtained. The undesired effect obtained due to the presence of Al is thus eliminated. Furthermore, the corrosion properties of TiN exceed even those of titanium. The good friction and wear properties of TiN have also been documented. Thanks to the invention, therefore, properties, sufficient mechanical strength (ultimate stress limit, B-module, ductility), desired corrosion and biocompatibility properties, as well as requisite tribological properties (wear, friction) have been combined for the joint-prosthesis application.

The method according to the invention also enables Ti-6Al-4V to be used in valve components and pump cylinders.

Valve and pump components made of titanium and titanium alloys are often used in the biotechnical and chemical industries. The problem of uncontrolled friction and wear properties is equivalent here to that in joint prostheses. From the strength aspect it is often possible to use Ti. However, problems arise in machining this material—turning, milling and especially finishing the surface. The alloy Ti-6Al-4V, on the other hand, is considerably easier to machine and thus also to obtain a reasonable surface finish, thereby creating the conditions for obtaining a surface which, from the friction, wear and sealing aspects, is necessary in order to avoid leakage and malfunction. In this case also Al is all undesired element from the corrosion aspect (precipitation). A titanium nitride layer according to the invention combines mouldability and machinability with excellent friction, wear and corrosion properties.

We claim:

1. A method for producing an integral continuous, uniformly distributed nitride layer between 0.5 and 10  $\mu$ m having a high degree of purity in the surface of objects formed of titanium and titanium alloys, which nitride layer has a hardness of approximately 2000 HV<sub>0.05</sub> and improves the friction and wear properties, as well as the corrosion-proof and biocompatibility properties of the titanium or titanium alloys in that the nitride layer is depleted of alloy metals from titanium alloys, comprising the steps of subjecting an untreated object to treatment for 3 to 16 hours in a vacuum furnace to an atmosphere of high purity nitrogen gas at high velocity flow at a temperature of 650° to 1000° C. and a pressure below atmospheric pressure, after which the temperature is reduced.

2. A method as claimed in claim 1, wherein prior to treatment the untreated objects are heated under partial vacuum to the treatment temperature, while being subjected to a high flow of nitrogen in order to remove from the surface contamination layers and impurities which are desorbed during the heating process.

3. A method as claimed in claim 1 or 2 wherein the thickness is governed by controlling the treatment time and temperature.

4. A method as claimed in claim 1 or 2 wherein the treatment is performed in equipment at a high vacuum.

5. A method as claimed in claim 1 or 2 wherein the treatment is performed in equipment with accurate temperature control so as to obtain a long and uniform temperature profile.